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(54) MANUFACTURE OF EMULSIFIER-FREE, ANIONIC POLYURETHANE DISPERSIONS

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ABSTRACT OF THE DISCLOSURE:

Polyurethane ionomer dispersions are manufactured from aromatic and aliphatic diisocyanates. Leather coatings produced from the dispersions possess improved mechanical properties.

MANUFACTURE OF EMULSIFIER-FREE, ANIONIC POLYURETHANE DISPERSIONS

The present invention relates to a process for the manufacture of emulsifier-free, anionic polyurethane dispersions from which coatings with improved properties can be produced.

The manufacture of emulsifier-free, aqueous polyurethane dispersions by introducing ionic centers into the polymer molecule, dissolving the polymer in an aqueous organic solvent and removing the organic solvent is dislcosed in, for example, U.S. Patent 3,479,310 and Angewandte Chemie, 82/2 (1970), 53-90, Verlag Chemie GmbH Weinheim.

In addition, British Patent 1,339,357 discloses that in the above context polyhydroxy-compounds having a molecular weight of from 350 to 10,000 are particularly suitable as starting materials and equimolar addition products of the alkali metal salts of α-olefinic carboxylic acids with aliphatic di-primary diamines are particularly suitable for introducing the ionic centers. Dispersion may be effected in any desired manner but the preferred method is first to react the polyhydroxy-compounds of fairly high molecular weight with excess diisocyanate, in the melt, to give a prepolymer with isocyanate end groups, to take up the prepolymer in a water-miscible organic solvent which boils below 100°C and to add to this solution an aqueous solution of the diamine containing salt groups, followed by water. The organic solvent is then distilled off.

However, coatings produced from the dispersions thus obtained still suffer from certain shortcomings which interfere with their industrial use, especially as leather coatings. Thus, whilst it is true that if aliphatic or cycloaliphatic diisocyanates are used finely divided stable dispersions are obtained, the coatings obtainable therefrom are very soft and have a rubbery hand. In contrast, aromatic diisocyanates give relatively coarse disper-

sions which sediment readily, and the coatings produced therefrom have unsatisfactory strength and wear resistance.

It is an object of the present invention to provide polyurethane dispersions which do not suffer from the above disadvantages.

We have found that this object is achieved and that the above disadvantages can be eliminated if the polyurethane ionomers are synthesized from a combination of aliphatic or cycloaliphatic diisocyanates with aromatic diisocyanates, either by using first the aromatic diisocyanates and then the cycloaliphatic or aliphatic diisocyanates, or by using both simultaneously. The synthesis of polyurethane ionomers from these isocyanate combinations is not suggested by the art, particularly as the components are known to react at very different rates, and since the products are, surprisingly, superior to the conventional products obtained from either aliphatic or aromatic diisocyanates. The new products form finely divided, stable dispersions from which hard and at the same time tough coatings having excellent strength and wear resistance can be produced.

The object of combining aliphatic or cycloaliphatic diisocyanates with aromatic diisocyanates to synthesize the polyurethane ionomers of the invention is the incorporation of fairly long polar segments of aromatic diisocyanate and chain extenders into the polymer molecule. The polyurethane obtained then contains both segments of aromatic diisocyanate, separated from one another by fairly long chians of, for example, polyesters or polyethers, and chain extenders without salt groups, as well as segments of aliphatic or cycloaliphatic diisocyanate and chain extenders, which do contain ionic groups. This is an essential feature of the invention. Such a segmented molecular structure obtained by combining aliphatic or cycloaliphatic diisocyanates

and aromatic diisocyanates when manufacturing the dispersions leads to an advantageous combination of properties, ie. the dispersions are stable and finely divided and impregnations, coatings and films obtained from the dispersions have excellent mechanical properties. The above disadvantages of the conventional products are thereby overcome.

Accordingly, the present invention relates to a process for the manufacture of emulsifier-free, aqueous polyurethane dispersions from

A) dihydroxy-compounds having a molecular weight of from 500 to 5,000,

B) diisocyanates,

C) water-soluble salts of aliphatic aminocarboxylic or aminosulfonic acids (preferably diaminocarboxylic or diaminosulfonic acids) containing at least one hydrogen atom bonded to a nitrogen atom but preferably two hydrogen atoms bonded to different nitrogen atoms and

D) compounds without salt groups, possessing two hydrogen atoms which are reactive toward isocyanate groups, and having a molecular weight of less than 300, as chain extenders, by forming initially a solution or dispersion of the polyurethane in an aqueous-organic solvent mixture and then removing the organic solvent(s), in which process the diisocyanate component (B) employed to from the polyurethane includes both an aromatic diisocyanate and an aliphatic or cycloaliphatic diisocyanate, the proportion of cycloaliphatic or aliphatic diisocyanate being from 10 to 50 mole %, and in the formation of the polyurethane either the aromatic diisocyanate is employed first and the aliphatic or cycloaliphatic diisocyanate thereafter, or both are employed simultaneously.

Suitable dihydroxy-compounds (A) are the conventional

polyesters, polyethers (with the exception of ethylene oxide homopolymers), polythioethers, polylactones, polyacetals, polycarbonates and polyester-amides with 2 terminal aliphatic hydroxyl groups. The molecular weights of these dihydroxy-compounds should be from 500 to 5,000, the range from 750 to 3,000 being particularly advantageous. Of course, mixtures of these dihydroxy-compounds of fairly high molecular weight may also be employed. Minor amounts of hydroxy-compounds with an average of more than two hydroxyl groups per molecule may or may not be present. However, if they are present, they should be employed only in such propertions that the overall functionality does not exceed a mean value of 2.2. The use of dihydroxy-compounds is however normally preferred. The mean number of hydroxyl groups per molecule must on the other hand not be less than 2.

Suitable diisocyanates (B) are the conventional aliphatic, cycloaliphatic and aromatic diisocyanates, eg. 1,4-butane diisocyanate, 1,6-hexane diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, cyclohexane diisocyanate, methylcyclohexane diisocyanate, isophorone diisocyanate, xylylene diisocyanate, 4,4'-diisocyanatodiphenylmethane, 4,4'-diisocyanatodicyclohexylmethane, 2,4- and 2,6-toluylene diisocyanate and their industrial mixtures of isomers. Mixed aliphatic-aromatic diisocyanates can also be used, in place of the purely aliphatic diisocyanates, for the process according to the invention. The molar ratio of the aliphatic or cycloaliphatic diisocyanates to the aromatic diisocyanates is advantageously from 1:1 to 1:9 and preferably from 1:2 to 1:6.

Suitable water-soluble salts of aliphatic aminocarboxylic acids or aminosulfonic acid (C) are disclosed, above all, in British Patent 1,339,357, but also, for example, in British Patent 1,329,565. They are preferably alkali metal salts, especially

sodium and potassium salts, of the adducts of lower aliphatic di-primary diamines, eg. ethylenediamine, with unsaturated carboxylic acids, eg. acrylic acid, methacrylic acid, crotonic acid or maleic acid, as well as alkali metal salts of lysine. In general, compounds which have two hydrogen atoms bonded to different nitrogen atoms and have only one salt group in the molecule, ie. compounds which, though they make the product dispersible, do not make it excessively hydrophilic, and which furthermore can act as chain extenders, are preferred. The alkali metal salts of the adducts of propanesultone with aliphatic di-primary diamines are also very suitable. They are used in such amounts that the total polyurethane composition contains from 0.02 to 1% by weight of $-CO_2^-$ or $-SO_3^-$ groups (the weight of the cation being left out of account).

Suitable low molecular weight chain extenders (D) without salt groups and having molecular weights of less than 300 are the conventional glycols, eg. ethylene glycol, propylene glycol, butane-1,3-diol and butane-1,4-diol, hexanediol, neopentylglycol, cyclohexanediol, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,2-bis-(4-hydroxyethoxyphenyl)-propane, diethylene glycol and dipropylene glycol, diamines, eg. ethylenediamine, hydrazine, piperazine, isophoronediamine, toluylenediamine, diaminodiphenylmethylene, N,N'-dimethylethylenediamine and aminoalcohols, and under certain circumstances also water. It is true that formally aminoalcohols and primary diamines have more than two hydrogens capable of reacting with isocyanate groups, but in fact they behave only as bifunctional compounds toward isocyanate groups under conventional reaction conditions, and it is this which matters.

The isocyanate groups and the hydroxyl and amino groups capable of reacting with isocyanate are generally employed in about equivalent molar ratios. The ratio of the number of iso-

cyanate groups to the number of total hydrogen atoms capable of reacting with isocyanate will generally be from 0.9 to 1.2, preferably from 1.0 to 1.1.

Components A, B, C and D are generally employed in such molar ratios that the ratio of the fairly high molecular weight hydroxy-compounds (A) to the sum of the diisocyanates (B) and to the sum of the compounds (C) containing salt groups and the low molecular weight chain extenders (D), ie. A;B:(C+D), is from 1:2:1 to 1:14:13. The range from 1:4:3 to 1:10:9 is particularly advantageous. These figures apply to the preferred case where component C is bifunctional ie. possesses two hydrogens bonded to different nitrogens. For other cases, the figures alter appropriately.

The conventional known catalysts, eg. dibutyl-tin dilaurate, tin-II octoate or 1,4-diazabicyclo-(2,2,2)-octane, may be used to accelerate the reaction of the diisocyanates.

The polyurethane compositions are manufactured in the conventional manner by reacting the fairly high molecular weight polyhydroxy-compounds with the diisocyanates and the low molecular weight chain extenders without salt groups, under atmospheric or superatmospheric pressure, in the melt or in the presence or absence of a water-miscible, inert organic solvent which boils below 100^{o}C, to give a prepolymer with terminal isocyanate groups.

The aromatic and aliphatic or cycloaliphatic diisocyanates (B) to be used according to the invention can be reacted either as a mixture with one another or successively, in the stated sequence, with the fairly high molecular weight dihydroxy-compounds (A) and the low molecular weight chain extenders (D). Because of the different reactivity of the two diisocyanates it frequently suffices to employ the diisocyanates as a mixture with one another. If they are reacted successively with the hydroxy-compounds A and D,

it is essential, according to the invention, to employ the aromatic diisocyanate first and the aliphatic or cycloaliphatic diisocyanate thereafter, to ensure that the reaction product possesses central segments of aromatic diisocyanate and chain extender (D) and terminal aliphatic or cycloaliphatic isocyanate groups. If the reaction of the two diisocyanates is carried out stepwise, it is not essential that the aromatic diisocyanate should have reacted completely before the aliphatic or cycloaliphatic diisocyanate is added; instead, it is frequently possible to add the aliphatic or cycloaliphatic diisocyanate at a point in time at which only a part of the aromatic diisocyanate has reacted.

The resulting polyurethane with terminal aliphatic or cycloaliphatic isocyanate groups may or may not be diluted, or further diluted, with a water-miscible solvent which boils below 100°C and is inert toward isocyanate groups; after dilution, if any, the polyurethane is mixed, generally at from 20 to 50°C, with a preferably aqueous solution of any of the salts of aliphatic aminocarboxylic acids or aminocarboxylic acids or aminosulfonic acids referred to under C. The reaction of the salts with the isocyanate groups takes place spontaneously and results in chain lengthening if the said salts contain more than one N-H group per molecule. Water is stirred into the solution of the resulting polyurethane, possessing salt-like groups as structural units, and the organic solvent is removed by distillation.

This gives finely divided, stable dispersions which can, if required, be concentrated by evaporation. In general, solvent-free latices having a solids content of from 30 to 50% are preferred.

Suitable low-boiling solvents are polar solvents which are inert toward isocyanates, boil below 100°C and are water-miscible, eg. acetone, tetrahydrofuran or methyl ethyl ketone.

This dispersions may be manufactured in accordance with,

for example, the following general instructions: the fairly high molecular weight, predominantly difunctional, hydroxy-compounds (A) are first dehydrated at 120°C for 30 minutes under reduced pressure from a waterpump; they are then mixed with the chain extenders free from salt groups, (D), and reacted, in the presence or absence of solvents, with a mixture of the two diisocyanates (B), or first with the aromatic diisocyanate and then with the aliphatic or cycloaliphatic diisocyanate, at from 50 to 130°C, to give a prepolymer with terminal isocyanate groups. The material is then diluted with solvent (or further solvent), to give a solution of from about 30 to 50% strength. A solution of the alkali metal salt of the diaminocarboxylic acid or diaminosulfonic acid in water is then added to the prepolymer solution. After completing the reaction at from 20 to 50°C, the calculated amount of water corresponding to the desired solids content of the dispersion to be produced is added and the solvent is distilled off under reduced pressure.

The dispersions thus obtained are fine and are stable for more than 6 months even at tropical temperatures. They can be processed by conventional methods to give films, sheets, coatings, finishes and impregnations, with a great variety of substrates. The dispersions are particularly suitable for leather coating. They have excellent adhesion to leather, are elastic, strong, tough and resistant to mechanical stress, and impart a pleasing hand.

Depending on their intended use, the polyurethane dispersions may also be combined with conventional modifiers and additives, eg. crosslinking agents, plasticizers, pigments, fillers and the like. They can also be blended with suitable dispersions of natural or synthetic polymers, eg. nitrocellulose.

In the Examples and Comparative Experiments, parts and percentages are by weight.

EXAMPLE 1

203 parts of a commercial polyester obtained from adipic acid, hexanediol and neopentylglycol and having an OH-number of 55 are dehydrated for 30 minutes in a stirred flask at 130°C under 20 mm Hg. The polyester is cooled and dissolved in 200 parts of acetone, and 40.5 parts of butane-1,4-diol are added. A mixture of 69.7 parts of toluylene diisocyanate (isomer ratio 2,4/2,6 = 80/20) and 33.6 parts of hexamethylene diisocyanate, as well as 0.02 part of dibutyl-tin dilaurate, are then added. After stirring for 3 hours at 60°C, the mixture is diluted with 300 parts of acetone and cooled to room temperature. 19.3 parts of a 40% strength aqueous solution of the equimolar addition product of ethylenediamine with sodium acrylate are then stirred into the resulting solution of the prepolymer. After 20 minutes, 500 parts of water are added dropwise and the acetone is then distilled off under reduced pressure.

A very fine, stable dispersion is obtained, which shows no tendency to sediment even on prolonged storage. If the dispersion is dried on glass plates, clear, very glossy and very tough films are obtained, which have a tensile strength of 330 kp/cm^2 and an elongation at break of 720%, both measured in accordance with DIN 53,504.

COMPARATIVE EXPERIMENT 1a

Using the method described in Example 1, 203 parts of the polyester employed there are dehydrated, dissolved in acetone and mixed with 36 parts of butane-1,4-diol. The amount of the butanediol chain extender is here reduced, compared to Example 1, by the same number of moles as the amount of chain extender containing salt groups is increased. The total number of moles of chain extenders is accordingly the same in both experiments. After adding 104.4 parts of toluylene diisocyanate (80/20 isomer

mixture) and 0.02 part of dibutyl-tin dilaurate, the experiment is continued as described in Example 1, except that twice the amount (15.4 g, dissolved in 23 g of water) of the chain extender containing salt groups (an adduct of ethylenediamine with sodium acrylate) is employed.

The dispersion obtained after distilling off the acetone is very coarse in spite of the salt group content being twice that of Example 1, and starts to sediment immediately. If the salt group content was lower, such sedimentation would of course be even more pronounced. The dispersion is therefore unusable for practical purposes.

COMPARATIVE EXPERIMENT 1b

Comparative Experiment 1a is repeated with an equimolar amount (100.8 parts) of hexamethylene diisocyanate in place of toluylene diisocyanate.

The propolymer becomes insoluble in acetone after a short time, and precipitates. A dispersion cannot be obtained.

If no butane-1,4-diol is employed as the chain extender and, accordingly, only 43.8 parts of hexamethylene diisocyanate are employed instead of 100.8 parts, whilst otherwise retaining the same procedure, a fine stable disperison is obtained, but this dispersion gives coatings which are very soft and have a rubbery hand, and are therefore unsuitable for most purposes.

COMPARATIVE EXPERIMENT 1c

241.5 parts of the polyester from Example 1 are degassed and reacted at 60°C with 36 of toluylene diisocyanate (TDI 80). The product is diluted with 700 parts of acetone and a mixture of 50 parts of water, 3.76 parts of ethylene-diamine, 4.26 parts of propanesultone and 19.6 parts of 10% strength aqueous sodium hydroxide solution is added. 360 parts of desalinated water are then added dropwise and the acetone is distilled off under reduced

pressure.

The dispersion obtained sediments after only a few hours.

EXAMPLE 2

401 parts of a commercial polyester obtained from adipic acid and ethylene glycol, and having a molecular weight of 2,000, are dehydrated and then diluted with 124.9 parts of neopentylglycol and 230 parts of acetone. 325 parts of 4,4'-diisocyanatodiphenylmethane and 44.5 parts of isophorone diisocyanate are then added, whilst stirring, and after the addition stirring is continued for one hour. The mixture is diluted with 900 parts of acetone and cooled to room temperature, and 38.5 parts of a 40% strength aqueous solution of the equimolar adduct of ethylenediamine with sodium acrylate are stirred in. After 30 minutes, 1,350 parts of desalinated water are slowely added dropwise and the acetone is stripped off under reduced pressure.

A very fine, stable dispersion having a solids content of about 40% is obtained. Samples coated onto glass plates dry at room temperature to give tough films which have a tensile strength of 24 N/mm^2 and an elongation at break of 430%, measured according to DIN 53,504, and a tear propagation resistance, measured according to DIN 53,775, of 56 Kp/cm.

COMPARATIVE EXPERIMENT 2a

Example 2 is repeated under identical conditions except that instead of the isophorone diisocyanate an equimolar amount, ie. 34.85 parts, of toluylene diisocyanate (TDI 80) is employed.

The dispersion obtained begins to sediment after only a few hours and a thick sediment forms overnight. Accordingly, the dispersion produced with 2 aromatic diisocyanates is unusable for practical purposes.

EXAMPLE 3

Example 2 is repeated except that instead of the polyester

400 parts of polytetrahydrofuran of molecular weight 2,000 are employed. The water is added at 50°C and in addition 500 parts of tetrahydrofuran are also introduced.

A fine, stable dispersion is obtained, which dries at room temperature to give tough, hazy films. The films are found to have a tensile strength of 45.3 N/mm^2, an elongation at break of 385% and a tear propagation resistance of 66 kg/cm.

EXAMPLE 4

509 parts of a commercial polyester obtained from adipic acid, hexanediol and neopentylglycol and having a mean molecular weight of 2,000 are dehydrated, 112.6 parts of butane-1,4-diol and 230 parts of acetone are added, and the mixture is stirred with 241.6 parts of toluylene diisocyanate (TDI 80) for 90 minutes, with the acetone boiling gently. 42.06 parts of hexamethylene diisocyanate and 0.2 part of dibutyl-tin dilaurate are then added stirring is continued for 90 minutes. The batch is then diluted with 900 parts of acetone, and at 40°C 63.3 parts of a 32.8% strength aqueous solution of sodium lysinate are stirred in. After 20 minutes, 1,250 parts of desalinated water are slowly added dropwise, whilst stirring, and the acetone is distilled off under reduced pressure.

A fine, very stable dispersion having a solids content of 40% is obtained. Even after standing for 6 months at room temperature, no sediment has formed. Samples coated onto glass plates dry at room temperature to give clear, very glossy and very tough films which have a tensile strength of 37 N/mm^2, and an elongation at break of 750%.

EXAMPLE 5

100 g (0.1 mole) of a commercial polyoxypropylenediol are dehydrated, mixed with 45.06 g of butane-1,4-diol and 50 g of acetone and reacted with 99.56 g of toluene diisocyanate (TDI 80)

at 55°C. After 30 minutes, 0.04 ml of dibutyl-tin dilaurate are added and 16.82 g of hexamethylene diisocyanate after one hour total reaction time, and stirring is continued for two hours. The mixture is diluted with 400 g of acetone, and 19.28 of the 40% strength aqueous solution of the adduct of ethylenediamine with sodium acrylate used in Examples 1 to 3 are added at 50°C. Then 500 ml of distilled water are added dropwise and the acetone is distilled off under reduced pressure.

A finely divided, stable dispersion is obtained which dries at room temperature to give hard and very tough films.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for the manufacture, by conventional methods, of emulsifier-free, aqueous polyurethane dispersions from A) at least one member from the group of polyesters, polyethers other than polyethylene oxide, polythioethers, polylactones, polyacetals, polycarbonates and polyester-amides having a molecular weight of from 500 to 5,000 and having two terminal hydroxyl groups,

B) diisocyanates,

C) water-soluble salts of aliphatic aminocarboxylic acids or aminosulfonic acids with at least one hydrogen bonded to nitrogen and

D) at least one compound from the group fo the glycols, diamines and aminoalcohols, having a molecular weight of less than 300, in a molar ratio of A:B:(C+D) from 1:2:1 to 1:14:13, in which a urethane prepolymer with isocyanate groups at both chain ends is first manufactured by reacting the compoenents A, B and D, at from 50 to 130°C, with or without a catalyst, as a melt or in a water-soluble inert solvent which boils below 100°C and is inert towards isocyanate, the solution of the prepolymer in one of the said solvents is then reacted by mixing with an aqueous solution of a sufficient amount of an aminocarboxylic acid salt or aminosulfonic acid salt (component C) that the finished polyurethane, which is now in the form of a dispersion, contains from 0.02 to 1% by weight of $-CO_2^-$ or $-SO_3^-$ groups, and the solvent is then distilled off to leave an aqueous dispersion, the improvement that the diisocyanate employed is a combination of aromatic and aliphatic or cycloaliphatic diisocyanates in which the proportion of aliphatic or cycloaliphatic diisocyanate is from 10 to 50 mole %, and that either the aromatic diisocyanate is employed first and the aliphatic

or cycloaliphatic diisocyanate is employed first and the aliphatic or cycloaliphatic diisocyanate thereafter, or both are employed simultaneously.

2. A process as claimed in claim 1, wherein a polyester or polyether other than polyethylene oxide is employed as component A.

3. A process as claimed in claim 1, wherein the material used as component A has a molecular weight of from 750 to 3,000.

4. A process as claimed in claim 1, wherein the aliphatic or cycloaliphatic diisocyanate and the aromatic diisocyanate employed as component B are employed in a molar ratio of 1:2 to 1:6.

5. A process as claimed in claim 1, wherein a water-soluble salt of an aliphatic diaminocarboxylic acid or a diaminosulfonic acid with at least one hydrogen on each of the two nitrogens is employed as component C.

6. Emulsifier-free aqueous polyurethane dispersions when manufactured by a process as claimed in claim 1.

7. Leather which has been coated with a dispersion as claimed in claim 6 and dried to remove water.